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Trace Analysis of Explosives from Complex Mixtures with Sample Pretreatment and Selective Detection

ABSTRACT: The analysis of explosive traces in different samples from criminal investigations is described. An important step for the analysis is sample preparation with solid-phase extraction. The analytical procedure is preferably performed with gas chromatography and nitro/nitroso-specific detection. The commercially available detection unit was modified. Possible solutions for the confirmation of the identity of an explosive trace are outlined.

KEYWORDS: criminalistics, explosives, chromatographic analysis, extraction, gas chromatography, TEA detection, solid-phase extraction, trace analysis, high-performance liquid chromatography

Trace analysis of explosives is a typical request in forensic chemistry for investigations involving criminal bombing. First, there is the search for the explosive material used at a bomb scene. This is done using debris from the scene and swabs taken from metal, glass, or wood pieces near the center of the explosion [1–5]. Depending on the surrounding area of the scene, the composition of the material that has to be checked may vary. Many chemical substances with possible interferences may accompany the explosive traces. Similar problems, often more inconvenient, arise during further investigations that follow a bomb scene, when cars or apartments are controlled and vacuum cleaner samples have to be checked for explosives. Such samples often contain complex mixtures of materials such as food, spices, or medicaments, in addition to the dust. All these substances from debris or vacuum cleaner samples normally are present at much higher concentrations than the explosives. Their chemical properties that are important in the analytical procedure, such as polarity or molecular weight, cover a wide range.

In Germany, the explosives usually used by terrorists are either self-made mixtures of chlorate and sugar or explosives containing nitro compounds. Chlorate/sugar mixtures may be recognized by the pieces of the container and by ion chromatography of the water extract. This paper describes the analysis of organic nitro explosives, especially nitroglycerine (NG), nitroglycol (EGDN), trinitrotoluene (TNT), dinitrotoluene (DNT), nitropenta (PETN) and hexogen (RDX). These substances are common ingredients in German military or commercial explosives.

The first step for trace analysis of explosives must be a sample preparation to increase the concentration of the explosives and eliminate interfering substances. This procedure will take most of the total analysis time and is essential for the success of the instrumental examinations. Sample precleaning may be done, for example, by extracting the material

with different solvents, by evaporation steps with gas-phase collection, or by solid-phase extraction. These methods are applied to obtain a fraction in which the explosives are selectively collected. The use of solvents of varying polarity is time and material consuming and results in the compounds accompanying the explosives fraction having a wide range of polarity. Gas-phase enrichment of explosives delivers a number of compounds with vapor pressures in the same region as explosives, while substances such as PETN or RDX with low vapor pressures are difficult to collect. Solid-phase extraction offers the possibility for cleanup of a solution obtained by one-step solvent extraction. The result is a concentrated fraction with a narrow range of compounds of polarity similar to that of the explosives. If the analysis of that fraction is performed with a chromatographic system and a selective detector, a successful trace analysis of explosives is possible.

Experimental Section

Solid-Phase Extraction

The SPE columns were 500-mg RP18 (3-cm) columns from ICT Germany. Conditioning was performed with three volumes of methanol and one volume of water. The original sample, whether dust or swabs, was extracted in a soxhlet extractor with acetone for at least 2 h. The acetone was slowly evaporated on a water bath at 50°C. The sample was then dissolved in acetone and diluted 1:10 with water. It was washed with three volumes of methanol/water (1:4). The elution was performed with three volumes of methanol. The methanol was evaporated and the sample was dissolved in a small volume of acetone for gas chromatography/thermal energy analyzer (GC-TEA) or acetonitrile for high-performance liquid chromatography (HPLC).

Gas Chromatography

The gas chromatograph was a Varian 3400 with split/splitless injection and a megabore injection port. The detector was a thermal energy analyzer (TEA) from Thermedics, modified as described. The original pyrolysis unit was replaced by a tube oven from Heraeus, Type RO 4/25. The pyrolysis temperature of the oven was 900°C. The columns were 15 m DB5 megabore (530 μm) with a 1.5-μm film thickness for the first series of experiments and 8 m DB5 (250 μm) with a 0.25-μm film thickness for the last experiments. The column polarity change was done by means of a megabore DB225 and a capillary DB17.

Liquid Chromatography

The HPLC equipment consisted of a modular system from LDC Analytical. The column was a Lichrospher RP18 (125 by 4.6 mm). The eluent was methanol/water (47:53) with a flow rate of 1 mL/min. Ultraviolet (UV) detection was performed at a wavelength of 210 nm.

Results and Discussion

The routine analysis of explosive traces, as with all analytical procedures, should be as simple as possible because low amounts of the substance may be lost if there are several sophisticated steps during the process. Another reason is the time pressure in forensic work, because the police have to take measures as soon as possible and one of the first questions after a bomb detonation concerns the identification of the explosive used.

A powerful improvement in our laboratory was the installation of a chemoluminescence detector (TEA) in combination with gas chromatography [6]. This equipment responds selectively to nitro and nitroso compounds, so that sample preparation can be handled more easily. In combination with the GC-TEA the fastest step in the laboratory procedure is the direct injection of the concentrated and filtered acetone extract into the gas chromatograph. In the beginning, the injection was done on a megabore capillary column, coated with a phenylmethylpolysiloxane (5% phenyl). Instead of selective detection, often a number of unidentified peaks were observed, but the resolution was sufficient to recognize the explosive compounds. Another more serious problem arose after about five injections or sometimes after only one injection, when the sensitivity for PETN and RDX decreased, and RDX showed a very poor peak shape. Figure 1 shows the injection of a standard after the analysis of a real sample. The peak of PETN in this chromatogram (15 min) has totally disappeared. That problem did not occur when only the pure standard solution was injected. It must have been caused by contamination of the column by accompanying substances in the real sample. If approximately 20 cm are cut from the beginning of the column, the old sensitivity is obtained again for the next few injections. It is believed that highly polar compounds with low vapor pressures contaminate the inner surface of the beginning of the column. This contamination must have catalyzed the decomposition of PETN and RDX at the higher temperatures needed for the evaporation of these compounds, or the contamination had strongly adsorptive properties for the two explosives. Decomposition was noted especially for PETN, when a peak at a lower retention time, just before EGDN, was observed, together with a decreased peak height of PETN. The direct injection procedure was not satisfactory because it was column consuming and required column testing after nearly each injection. Therefore, a sample cleanup procedure with solid-phase extraction was introduced.

Initially using solid-phase extraction, a two-step procedure with reversed phases and normal phases [7] was successfully applied, but because highly polar compounds seemed to be the problem, the cleanup procedure was simplified. The most effective concentrating and cleaning step uses a C18 SPE column with 500 mg of material in it. Into this column the concentrated acetone extract diluted with water (1:10) is purged and is washed with methanol/water (1:4 v/v). After washing, the explosives fraction simply is eluted with pure methanol. Because the extract may be highly concentrated, it is important to have a SPE column with 500 mg of material. During the washing step, all highly polar compounds are eluted and the explosives as well as lipophilic compounds are retained. The final recovery of the explosives fraction in our laboratory is done with pure methanol. Usually, water is added to the eluent in the last step. With water content in the methanol, the more lipophilic explosives, such as PETN, often remain on the SPE column and are lost for the analysis. The addition of water is done to leave the interfering lipophilic substances on the SPE column. But, because the volume of methanol needed to elute the explosives fraction is very small, most of the strong hydrophobic substances from the matrix cannot be coeluted anyway.

Recovery data for the early eluting RDX and the last eluting PETN are given in Table 1. These two compounds may serve as border marks for the polarity range in reversed-phase behavior, because RDX is the first eluting compound on a HPLC column under reversed-phase conditions and PETN is the last eluting. The other important explosives, such as EGDN, NG, or those in the nitroaromatics range are in between these two.

The recovery data for the pure standard without the matrix represents the application ability of the method. The smallest recovery was found for RDX, which is the most polar compound. It is possible to enhance the method for RDX, but elution of polar interferences will become worse, so that there is no advantage in lessening GC contamination. More interesting than the pure standard are the experiments with real samples. To test the matrix influence on solid-phase extraction, three samples from dust, car explosion
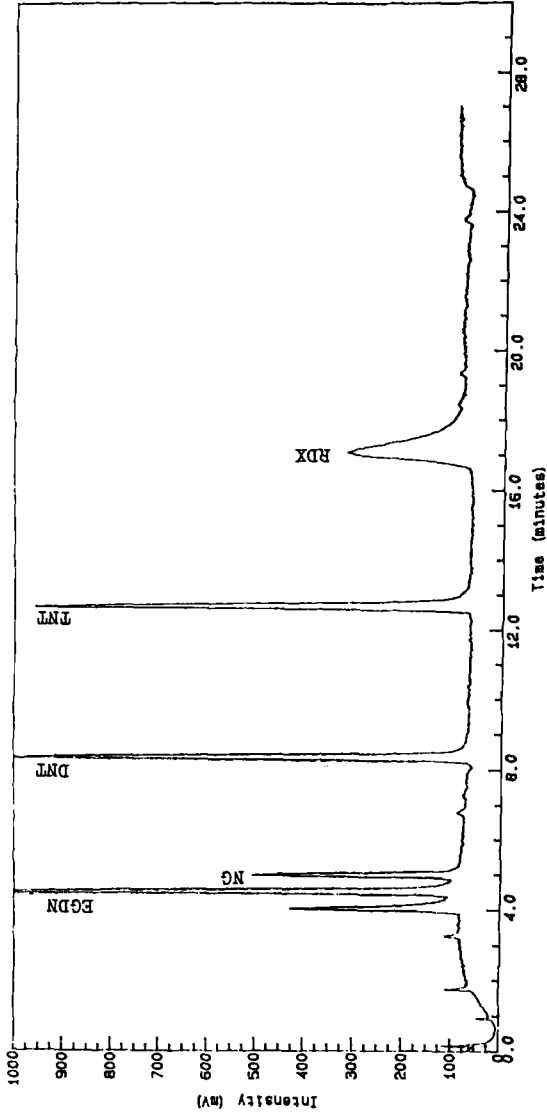
FIG. 1—*GC-TEA chromatogram of a mixture of explosives after the analysis of a real sample. RDX has a bud peak shape. PETN (15 min) has disappeared. Column = 15-m DB5 [0.53-mm inside diameter (ID)]; explosive amounts = 5 ng each.*

TABLE 1—*Recovery data for explosives after solid-phase extraction.*

	RDX, %	TNT, %	PETN, %
Standard mixture	72	82	94
Real Sample A	108	105	98
Real Sample B	74	61	106
Real Sample C	79	54	72

debris, and building debris were evaluated and spiked with the explosives standard. In one experiment, the recovery data were even higher after SPE than before it, possibly because of difficulties in quantitation of complex chromatograms. The overall recovery was always higher than 50% and was good enough for qualitative work, especially with enhanced clearness and response behavior.

The effect of the cleanup procedure can be seen in Fig. 2, where the 1st and the 16th on column injection of a real sample, spiked with a standard, without a portion cut from the GC column, are shown. The sensitivity and peak shape for both RDX and PETN, show the same behavior and the stability of the system is good enough for routine analysis.

The influence of solid-phase extraction on the HPLC chromatogram is not obvious. Only the very early eluting range near the injection peak obviously changes, the rest of the chromatogram remains nearly the same. This behavior is expected, because the cleanup procedure is like that for HPLC, and the exact polarity range of the interesting HPLC chromatogram must be recovered. The chromatograms of a spiked real sample before and after solid-phase extraction are shown in Fig. 3.

The solid-phase extraction is especially useful for the GC-TEA analysis. To get all the possible advantages in the trace analysis of explosives from both cleanup and selective detection, the GC-TEA equipment was modified. As described in the literature [8], the biggest problem, when the sensitivity of the GC-TEA is enhanced by the use of capillary columns with sharper peaks, is the electronic part of the TEA detector. Its amplifier is too slow for the fast capillary peaks because of the noise filtering system. The problem was circumvented by the replacement of the capacitor in the noise filter of the amplifier [9,10]. The pyrolysis interface of the TEA was removed and the GC capillary column was passed through a tube oven and directly connected to the TEA reaction cell.

These modifications improved the sensitivity of the GC-TEA equipment, but an interface problem arose from the replacement of the original oven by a tube oven. It is well known in GC, that cool zones at the end of the column lead to condensation of high-boiling-point compounds. To avoid that problem, the part of the capillary column between the GC and the tube oven was insulated against the outside with glass wool to keep the heat in the capillary column. The result was the loss of sensitivity for PETN and RDX with simultaneous peak broadening. Obviously, the insulation had the inverse effect of that intended. Figure 4 shows the typical Christmas tree effect when it was partly removed. The total removal of the glass wool and the direct placing together of the GC wall and the tube of the oven was the best solution.

By modification of the GC-TEA equipment, the sensitivity for each explosive is enhanced. The signal-to-noise ratio is approximately ten times higher. Total amounts of 50 pg of each explosive are clearly detectable. Therefore, traces in swabs or adherents on small particles in the nanogram level can be identified with the described method.

Confirmation of Identity

The identification of an unknown peak in the GC-TEA chromatogram is normally done by injection of a standard solution. The same retention time is a clear indication for the similarity. The chromatographic separation is selective for vapor pressure and

polarity. The detection is specific for nitro or nitroso compounds. There are only a very few substances giving a peak in the GC-TEA chromatogram at the same retention time. But, in spite of this, a second method is necessary to assure the identity of the explosive. This is particularly important for dust samples from cars or apartments, which may contain all kinds of substances. If the concentration is high enough, HPLC with UV detection (210 nm) may be the second method. The best choice is HPLC with selective and sensitive detection [11] for example, HPLC-photolysis-electrochemical detection [12]. The latter is in experimental evaluation in our laboratory at the moment. Liquid chromatography shows a big difference in elution behavior in comparison with gas chromatography, and peak assurance with HPLC and GC is unequivocal.

In the case of a low-level concentration, when the HPLC method is not sensitive enough, confirmation of identity may be done by replacing the GC column with another GC column of different polarity, for example, the phenyl(5%)-methylpolysiloxane is replaced by a phenyl(25%)-cyanopropyl(25%)-methylpolysiloxane-coated column. Having the same retention time change for the explosive and the believed substance in GC-TEA provides the certainty that both compounds are identical. Figure 5 demonstrates the confirmation of DNT, DNEB, and TNT in a real case by column change.

Confirmation by GC-MS is suitable for nitroaromatic compounds, because their mass spectra are characteristic, whereas the spectra of nitrate esters or nitramines are not typical enough to recognize them in the complex matrix. Difficulties may arise for the identification of PETN. The UV absorbance in HPLC even at 210 nm is very low and a PETN trace cannot be identified without doubt. Figure 6 shows the GC-TEA and HPLC analysis of a real sample with a trace of PETN. In the HPLC chromatogram, the peak for PETN is very small in relation to the others and cannot serve for identification. The change of the GC column in that case may give problems, because PETN is difficult to elute from GC columns with higher polarity without decomposition. But the temperature sensitivity of PETN may have an advantage. PETN decomposes at injector temperatures higher than 170°C in a split/splitless capillary injector. Decomposition is complete at 250°C. If the injector temperature is about 220°C, two characteristic peaks can be observed. One peak from the original PETN and another peak which eluted at an early retention time. This early eluting peak has the broad peak shape typical of a decomposition product. The effect is useful for the identification of PETN traces with GC-TEA. The normal injection is performed at 170°C, and if there is a peak at the PETN retention time, a second injection at 220°C is done. The relative decrease of the peak height and the formation of a peak at the lower retention time gives the assurance that PETN was in the sample. Figure 7 shows the behavior for a real sample that contained traces of PETN.

Conclusions

The trace analysis of explosives requires a careful analytical procedure. The most useful technique is GC analysis with nitro/nitroso-specific detection in combination with solid-phase extraction for the sample preparation. That method allows low level trace analysis of very complex samples. In spite of the high selectivity in preparation and detection, a second analytical method is necessary for confirmation of the results. HPLC with simple UV detection is not selective enough, so that changes in the GC method have to be applied at the moment. Introduction of a selective trace level detection in HPLC is planned for the future.
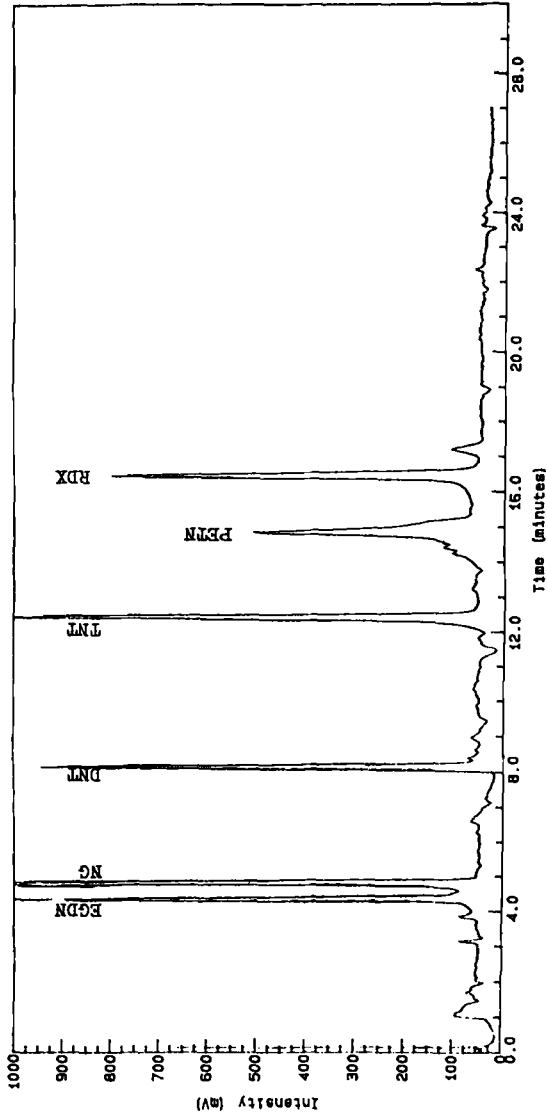
FIG. 2a—*The first injection of a real sample, spiked with a mixture of explosives. The sample has been prepared by solid-phase extraction. Column = 15 m DB5 (0.53 mm ID); explosive amounts = 5 ng each.*
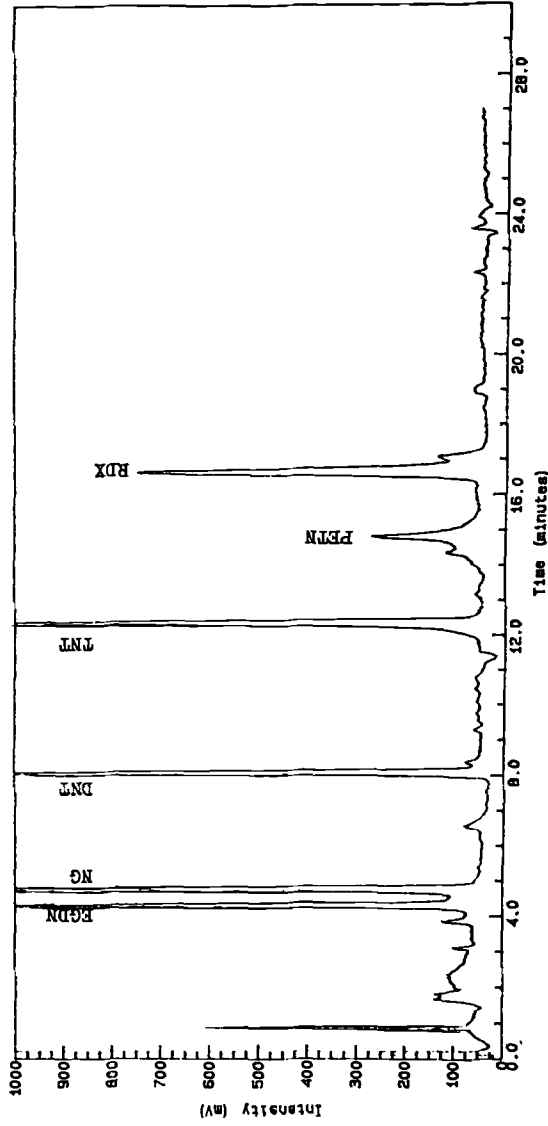
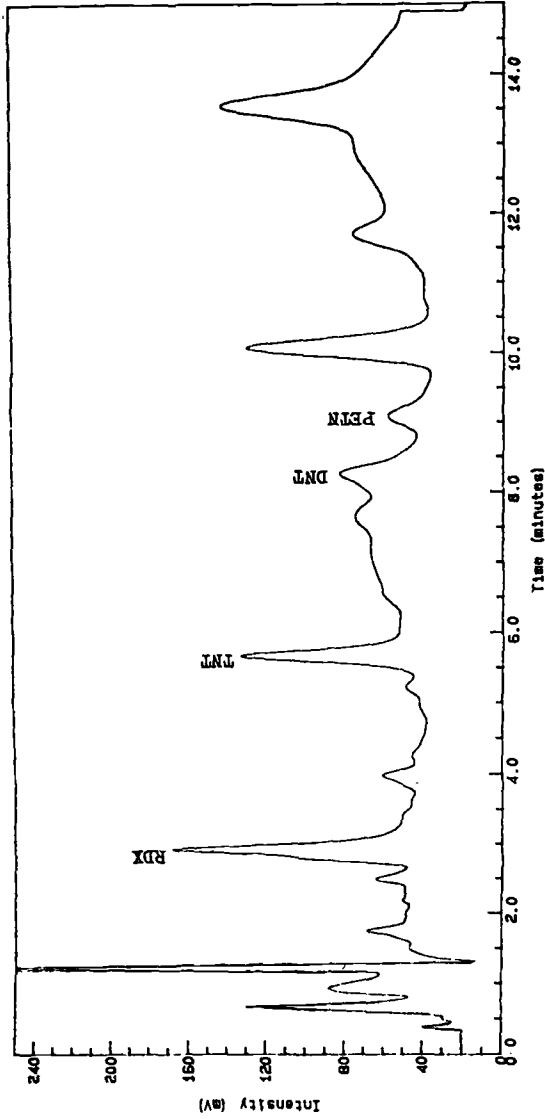FIG. 2b—*The 16th injection of the sample in Fig. 2a, under the same conditions.*

FIG. 3—*HPLC chromatogram with UV (210 nm) detection: (a) after solid-phase extraction of a real sample, spiked with a mixture of explosives. Column = Lichrospher RP18; eluent = methanol/water 47:53.*
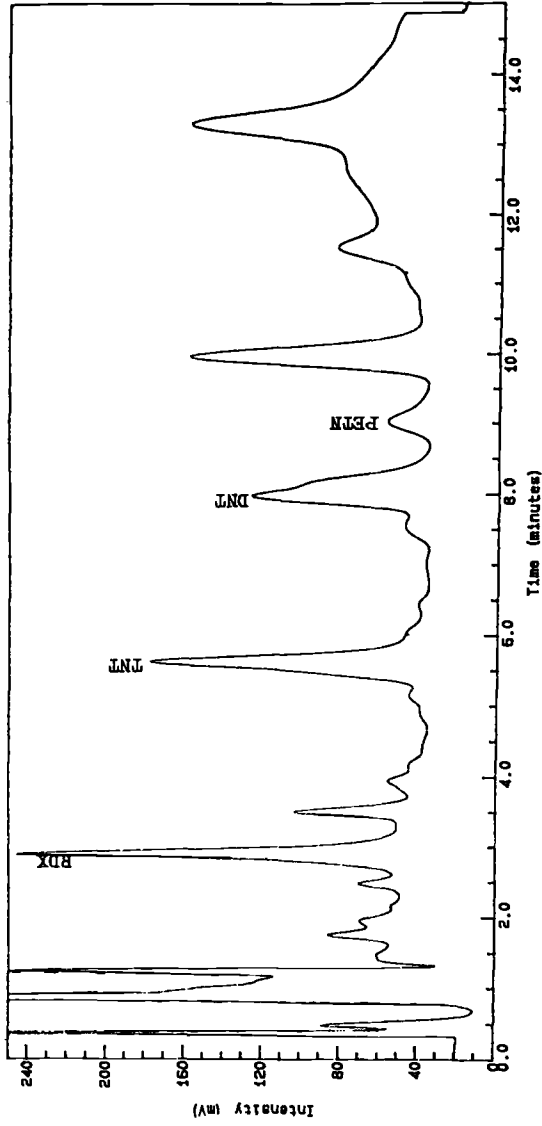
FIG. 3—*Continued*: (b) *before solid-phase extraction.*
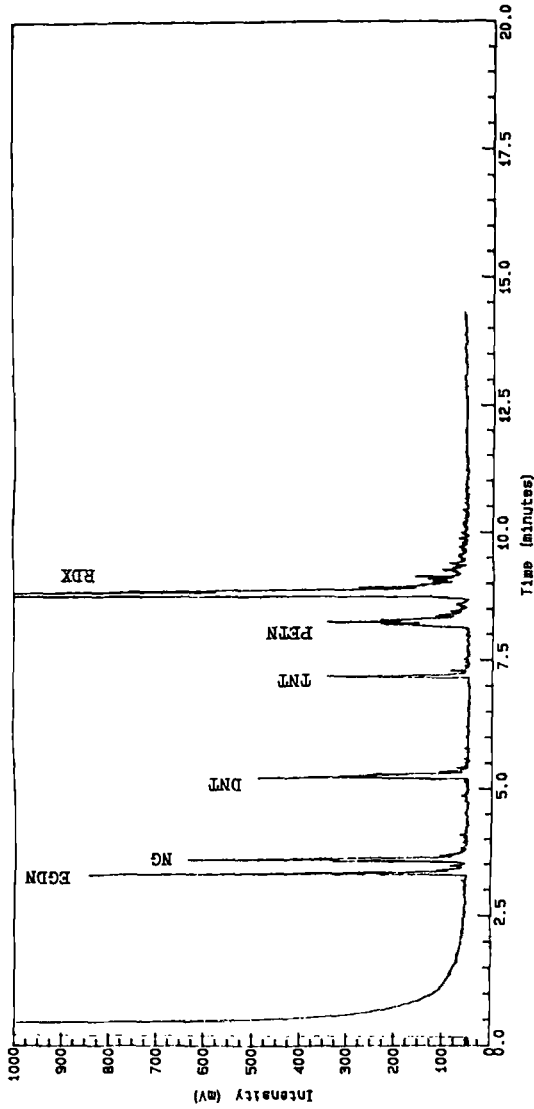
FIG. 4—*GC-TEA chromatogram after modification of the TEA amplifier and the TEA oven: (a) the condensing effect at the column end. Column = 8 m DB5 (0.25 mm); explosive amounts = 500 pg each.*
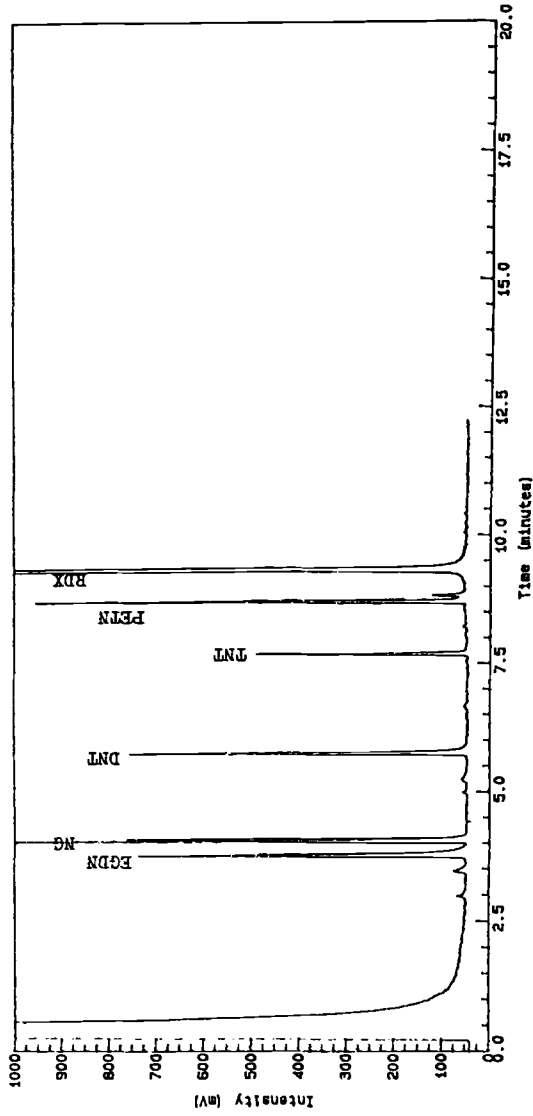
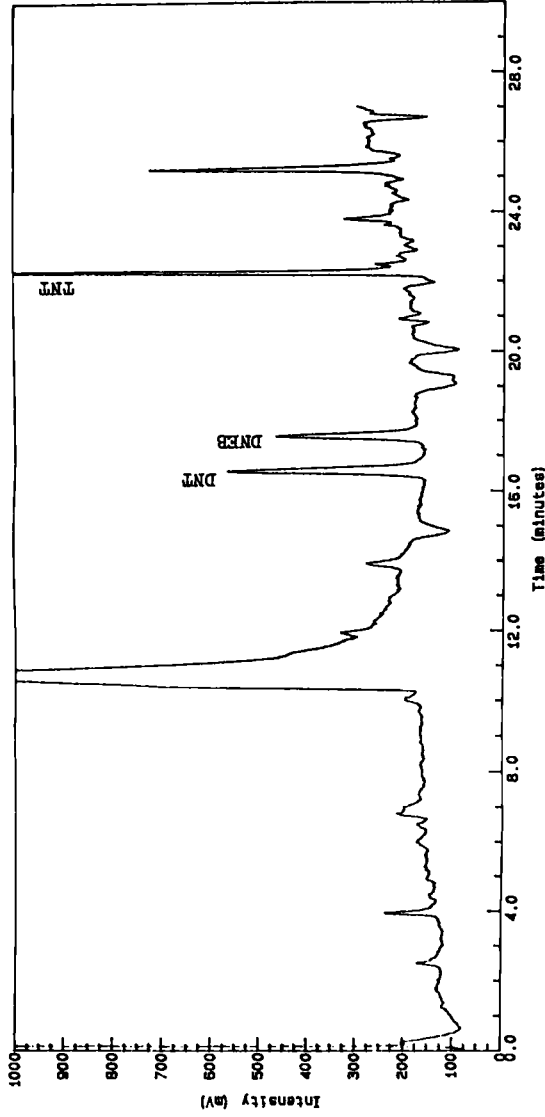FIG. 4—Continued: (b) the final capillary chromatogram.

FIG. 5—*Confirmation of identity with GC-TEA by application of columns of different polarity:* (a) *column = 15 m DB225 (0.53 mm).*
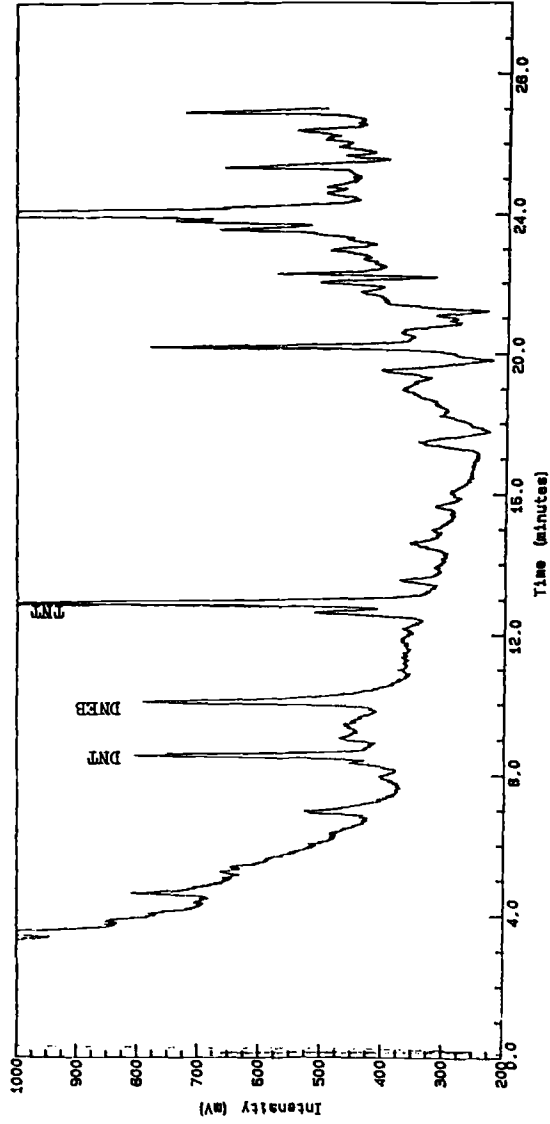
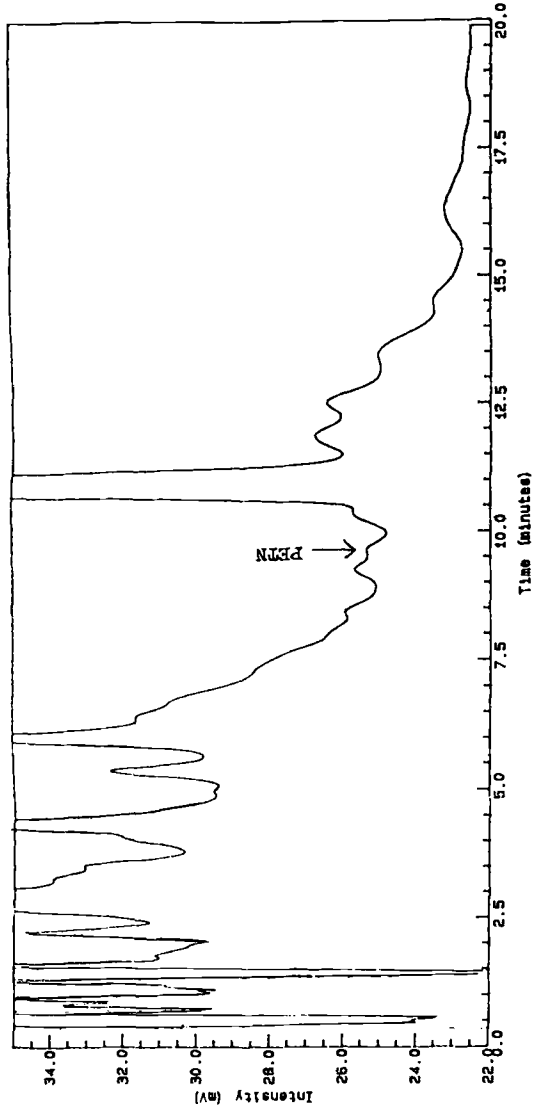FIG. 5—*Continued*: (b) *column = 15 m DB5 (0.53 mm)*.

FIG. 6a—*HPLC chromatogram of a real sample with traces of PETN. HPLC column = Lichrospher RP18; GC column = 8 m DB5 (0.25 mm).*
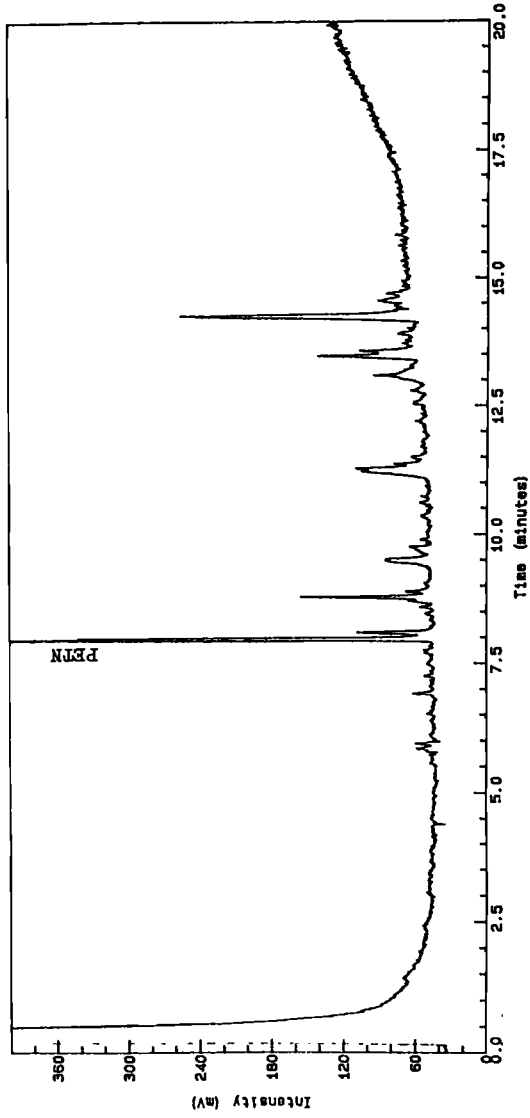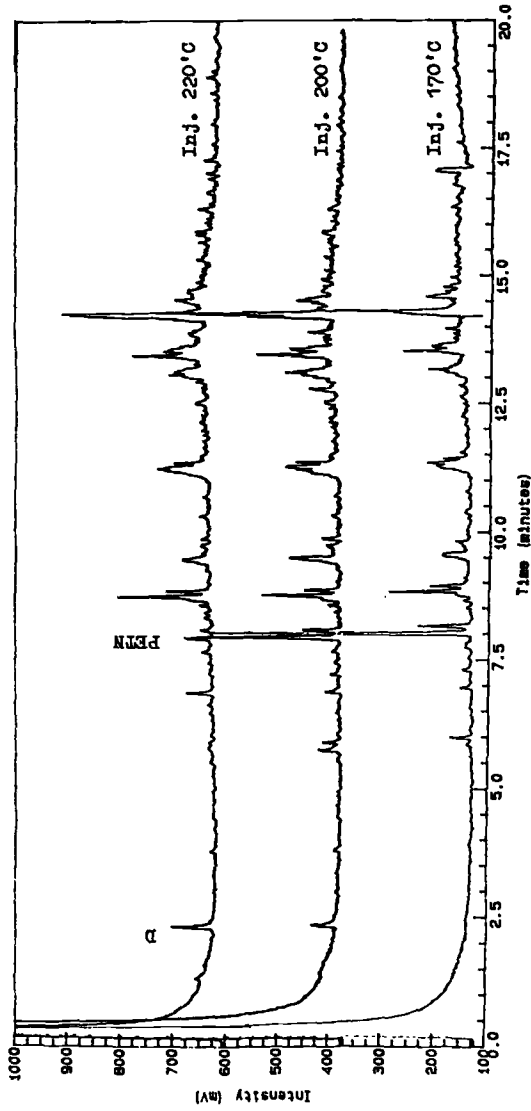
FIG. 6b—GC-TEA of the sample in Fig. 6a.

FIG. 7—Confirmation of a PETN trace by defined thermolysis in a split/splitless capillary injector. Column = 8 m DB5 (0.25 mm).

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